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ELECTRET PROPERTIES OF RADIATION-CHARGED PHOSPHATE GLASSES

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The process of formation of a surface charge in phosphate glasses depending on polarization conditions is investigated. A relationship is established between the chemical composition of glass and its capacity for forming internal electric fields under radiation for glasses of type $0.50P_2O_5 – 0.45RO – 0.05R_2O_3$.

The study of polarization phenomena in dielectrics is acquiring a growing significance, not only in the theoretical but also in the practical context. Of special interest are dielectrics capable of manifesting electret properties, i.e., capable of forming intense internal or external electric fields that are stable for a long time, for instance, as a consequence of accumulation of a volume electric charge. The domestic and foreign literature describes various instances of effective use of electrets in various sectors of engineering [1, 2]. Thus, the simplicity and low cost of electret condenser microphones stimulate their wide use in electronic equipment.

The molecular theory of the electret effect is not yet sufficiently developed, and the phenomenological theory relates the existence of charges in electrets to residual polarization. Models of the electret state have been developed for various dielectrics. A model has been constructed and analytically solved, which, in contrast to earlier known models, considers the case where the number of inherent carriers is small compared to the number of incorporated charges [3]. In this case, the incorporated carriers transfer to the volume, thus forming a relaxing volume charge. It is demonstrated that the relaxation of the charge proceeds against the background and under the effect of relaxation of the internal polarization of the electret.

Inorganic glasses are promising for the production of electrets, since their production technology allows samples of various configurations and sizes.

As a consequence of earlier studies [3], it was found that a necessary condition for producing electrets from glasses is heterogeneity of their structure, whereas distinctions in the nature of heterogeneity do not affect the process of formation of a stable field. Residual polarization in such materials is developed due to trapping of charges at the glass – crystal boundary (in glass ceramic materials) and the glass – glass boundary (in liquating borosilicate and borophosphate glasses). However, the physical mechanism of the electret effect in inorganic glasses and glass ceramics is on the whole not clarified. In any case, it is impossible to make a unique conclusion on the effect of a heterogeneous structural lattice on the electret properties of the specified materials.

The known ability of high-ohm polymer materials to form a volume charge under ionizing irradiation [2] is also inherent in phosphate glasses with a homogeneous structural lattice. Thus, there are published data on the ability of aluminophosphate glasses modified by oxides of alkaline-earth elements to accumulate a volume charge under the effect of an electron flow [4]. It is established that lower conductivity before irradiation and a higher vitrification temperature correlate with a higher value of the charge transmitted after irradiation [4, 5]. The specific volume resistance of glasses and the vitrification temperature grow with increasing lattice energy of oxides incorporated into the glass composition, i.e., the value of the accumulated charge is proportionate to the lattice energy of the glass. This fact is corroborated by the energy theory of ion crystals: crystals with a greater energy of the crystal lattice exhibit a greater accumulation of radiation energy.

It is established that the highest field intensity of a charge accumulated on a glass surface is achieved when the concentration of color center vacancies formed as a consequence of radiation is minimal, and as it keeps growing, the intensity is diminished [5, 6]. As the radiation resistance of glass, which is proportional to the glass lattice energy, increases, the surface charge density grows. The decreasing value of the charge in the process of radiation generation of vacancy color centers is related to the reactions between the latter and the PO_3^{2-} radicals, which act as traps for injected electrons.

We investigated the reaction between electron beams and glasses, whose composition is expressed by the sum of meta-

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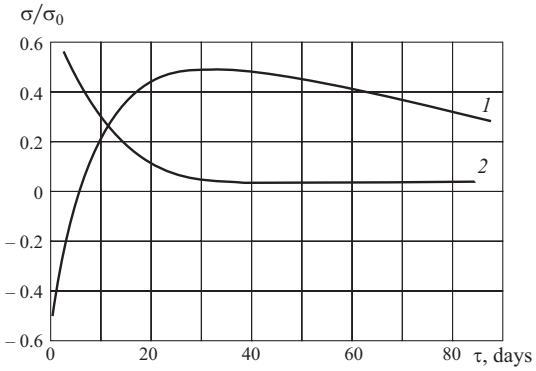

Fig. 1. Time dependence of surface charge density σ/σ_0 for phosphate glass electrets at field intensities over 10 kV/cm (*1*) and below 10 kV/cm (*2*).

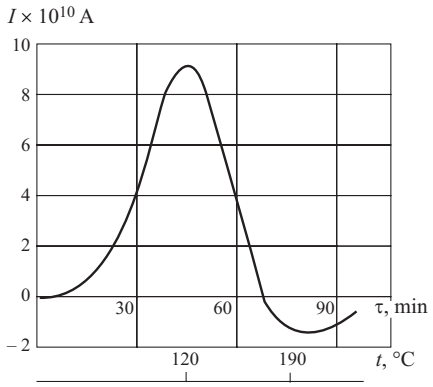

Fig. 2. Dependence of thermal depolarization current *I* on temperature *t*.

phosphates of alkaline-earth elements. The radiation was implemented using an electron beam with energy 1.0 and 1.5 MeV and flux density 5.0×10^{-8} and 3.1×10^{10} A/cm^2. The specific conductivity of glasses at 20°C ranged from 10^{-13} to 10^{-15} S/m depending on the glass composition. The glasses selected for study were clear, and no defects or indications of lamination of the structure were identified in them using an electron microscope.

The studies were performed on glass samples 25 and 40 mm in diameter and 1 – 5 mm thick using intensity from 5 to 50 kV/cm at temperatures from 20 to 250°C. The charge surface was measured using a vibrating electrode with compensation.

The volume charge was estimated using the thermal depolarization method, as well as the method of radiation probing of internal fields in materials, which is based on measurement of the increment of reverse electron scattering or determination of other parameters of the electron beams passing through dielectric materials irradiated on an accelerator.

Electric polarization was implemented in an electric furnace. The dielectric sample was first heated to a preset temperature, then the electric field was switched on, and the sample was held for 1.5 h at a constant temperature. The charges generated on samples were measured immediately after the end of the polarization process and again after specific time periods.

As a consequence of the performed studies, time dependences of variations in the surface density of electret charges generated under different conditions of polarization were obtained. Figure 1 shows some results of these studies. Under polarization in fields with intensity below 10 kV/cm and temperature 200°C, heterocharges arise in phosphate glasses, whose surface density decreases to one-tenth during the first 20 – 30 days, and then remains virtually constant for 2 months. Heterocharges generated in glasses in fields of higher intensities decrease to zero during 4 – 5 days, after which the sign of the charge is reversed and the charge density is preserved for 3 months.

Internal polarization was studied using the traditional thermal depolarization method with hold-down electrodes. Typical dependences of the discharge current on the temperature and duration of the process were registered with two maxima of opposite polarity: 90.0×10^{-10} A at a temperature of 120°C and $– 1.5 \times 10^{-10}$ A at 190°C (Fig. 2).

The experimental studies make it possible to determine the relationship between the chemical composition, the initial electrical parameters of glasses, and their ability to form intense internal electric fields under radiation. For instance, the delaying and scattering effect of an electric field on electron beams in phosphate glasses containing low-atom modifier oxides (magnesium and calcium) produces a 2 – 2.5-fold increase in reverse scattering coefficient, and the same coefficient in glasses containing barium and strontium oxides increases 1.3 – 1.5 times. The field intensity in the case of replacement of low-atom modifiers by high-atom ones drops from 2.2 MV/cm in magnesium-phosphate glass to 0.5 MV/cm in barium-phosphate glass.

Analysis of charged state stability indicates that, on the average, the period of electric field intensity in the considered glasses decreasing by half comprises 30 – 40 days, after which the field intensity remains virtually constant for several months.

The capacity for accumulation and conservation of charge is related to the structural peculiarities of energy bands in phosphate glasses and is determined by the existence of deep traps in the forbidden band. The band structure specifics are determined by the pentavalent phosphor cation, which forms together with oxygen a coordination tetrahedron in the glass structure.

A higher charge value is observed in glasses with a lower initial conductivity, and the highest charge is accumulated in glass of metaphosphate composition. The factor determining the value of accumulated charge is the energy of the glass structure. As the strength of the bonds grows, the inherent conductivity and the concentration of vacancy trapping centers decrease, and the accumulated charge increases.

The performed studies made it possible to develop new metaphosphate glasses of the type $0.50P_2O_5 - 0.45RO - 0.05R_2O_3$, which exhibit high reproducibility of their compositions in synthesis. The specified glasses are capable of accumulating electric charge and retaining it for a long period.

The electret state proved to be stable not only in laboratory conditions but also under the conditions of the open surface of a spacecraft [7]. The use of the developed glasses in space engineering makes it possible to increase the efficiency of protection of the elements of high-orbit spacecraft from electronic radiation, which will almost double the service life of spacecraft on the whole.

REFERENCES

1. A. N. Gubkin, *Electrets* [in Russian], Izd. Akad. Nauk SSSR, Moscow (1961).
2. G. A. Lushcheikin, *Polymer Electrets* [in Russian], Khimiya, Moscow (1976).
3. V. I. Arkhipov and A. I. Rudenko, "Relaxation of electret state in materials," *Fiz. Tekh. Poluprovodn.*, **10**, Issue 4, 729 – 734 (1976).
4. V. L. Auslender, V. N. Lazarev, and V. V. Tsetlin, "Experimental study of interaction between electron beams and high-ohm dielectrics," *Zh. Teor. Fiz.*, **53**(3), 514 – 517 (1983).
5. E. K. Zavadovskaya, V. A. Starodubtsev, B. V. Fedorov, and E. S. Kutukova, "The effect of the chemical composition of phosphate glasses on the value of the charge accumulated under electron radiation," *Neorg. Mater.*, **13**(1), 153 – 155 (1977).
6. A. A. Vorob'ev, E. K. Zavadovskaya, V. A. Starodubtsev, and B. V. Fedorov, *Fiz. Khim. Stekla*, **3**(1), 54 – 58 (1977).
7. M. M. Koltun and V. V. Tsetlin, "A study of stability of the charged state in optical coatings on solar cells in space," *Geliotekhnika*, No. 3, 44 – 47 (1985).